Contract Information

Contract Number	HR0011-04-1-0029
Title of Research	Spintronic Nanodevices Defined by Nanolithography
Principal Investigator	Dr. Charles J. O'Connor
Organization	University of New Orleans, New Orleans, LA 70148

FINAL TECHNICL REPORT – December 15, 2007

Purpose:

The purpose of this report is to document the results of the complete effort for this project, which was to explore the possibilities of employing nanoparticles, nanostructured thin films, and nanowires in spintronic nanodevice fabrication by using e-beam lithography techniques at AMRI-UNO.

Progress Summary

(1) Nanotransistors Defined through E-beam Nanolithography – Dr. Weilie Zhou

Our group has been focused on two directions during this project: one is semiconductor nanowires synthesis and one is nanotransistors fabrication using e-beam nanolithography. During the project period, we have been working on semiconductor nanowire synthesis, such as ZnO, SnO_2, In_2O_3, etc. and diluted magnetic semiconductor nanowire synthesis, such as Mn doped and Co doped ZnO nanostructures. Chemical vapor deposition and pulsed laser deposition have been set up by using this DARPA fund. A detailed nanostructure study has been investigated to study the synthesis condition and growth mechanism by XRD, SEM and TEM analysis. Physical properties, such as transport and magnetic measurements, have been performed to investigate the room and low temperature ferromagnetic properties. Detailed writing parameters of nanolithography, such as dose density, exposure time, size, features, photoresist, developing condition, lift-off, etc. have been studied and a solid data base for nanolithography patterning at AMRI has been established. Furthermore, diodes, field effect transistors, mechanic nanodevices have been successfully fabricated using e-beam nanolithography techniques. Spintronic nanotransistors based on nanowires are still under investigation. The nanodevices fabricated in our group can be used in chemical and biological nanosensors, NEMS, spintronics, and photovoltaic devices.

Publications

1. "Room-temperature Ferromagnetism of Mn Doped ZnO Aligned Nanowire arrays with Temperature Growth", J.J. Liu, K. Wang, M.H. Yu, **W.L Zhou**, Journal of

Applied Physics 102, 024301D (2007).

2. "Characterization of Diluted Magnetic Semiconductors of Co-doped and (FeCo)-codoped ZnO Nanostructures by Nanoprobe EDS Analysis", J. J. Chen, Y. Yan, A. West, J. J. Liu, and **W. L. Zhou**, Microscopy & Microanalysis 13 (Supp.) 737CD (2007).
3. "Fe-doped ZnO Nanowire Arrays Synthesized by Chemical Vapor Deposition", K. Wang, J.J. Chen, and **W.L. Zhou**, Microscopy & Microanalysis 13 (Supp.) 736CD (2007).
4. "Nanostructure and EELS Characterization of Diluted Magnetic Semiconductor Zn1-xCoxO Nanoneedles", **W.L. Zhou**, J.J. Chen, K. Sun, and L.M. Wang, **Microscopy & Microanalysis** 12, 1018CD, (2006). (Corresponding Author).
5. "Patterned Metal Nanowire Arrays from Photolithographically-Modified Templates" F. Li, Mo Zhu, C. Liu, **W.L. Zhou**, and J.B. Wiley, **J. Am. Chem. Soc.** 128, 13342 (2006).
6. "Magnetic Interaction in Co-doped SnO_2 Nano-crystal Powders" C.M. Liu, X.T. Zu, **W.L. Zhou, Journal of Physics: Condensed Mater**, 18 6001-6007, (2006).
7. "Fabrication of Mn Doped ZnO Diluted Magnetic Semiconductor Nanostructures by Chemical Vapor Deposition" J.J. Liu, M.H. Yu, and **W.L. Zhou**, **J. Appl. Phys.** 99, 08M119 (2006). (Corresponding author).
8. "Well-aligned Mn-doped ZnO Nanowires Synthesized by a Chemical Vapor Deposition Method", J. J. Liu, M. H. Yu, and **W. L. Zhou**, **Appl. Phys. Lett.** 87, 172505 (2005).
9. "Room-temperature Ferromagnetic Co-doped ZnO Nanoneedle Array Prepared by Pulsed Laser Deposition", J.J. Chen, M.H. Yu, **W.L. Zhou**, K. Sun, and L.M. Wang, **Appl**. **Phys**. **Lett**. 87, 173119 (2005).
10. "ZnO Nanostructures Fabricated through a Double Tube Vapor Phase Transport Synthesis" Y. X. Chen, M. Lewis and **W. L. Zhou**, **Journal of Crystal Growth** 282, 85 (2005).
11. Giant Negative Magnetoresistance of Spin Polarons in Magnetic Semiconductors-Chromium-doped Ti_2O_3 Thin Films, Z.Wang, Y. Hong, J. Tang, C. Radu, Y.Chen, L. Spinu, and **W.L. Zhou, Appl. Phys. Lett** 86, 1 (2005).
12. "E-beam Nanolithographically Patterned Metal Oxide Nanowire Arrays for Highly Sensitive Gas Sensors" L. Campbell A. D., D. Smith, G. May, L. Caliste, Y. Chen, and **W. L. Zhou**, **Microscopy & Microanalysis** 11, 1980 (2005).
13. "Electron Transport Property Measurement of Metal Oxide Nanowire Based Nanodevices Using Nanomanipulators In-Situ FESEM", **Weilie L. Zhou**, Mo Zhu

and Yuxi Chen, **Microscopy & Microanalysis**, 11, 1510 (2005).

14. "Multiple Branched SnO2 Nanowire Junction" **W.L. Zhou**, Y. Chen, L. R. Compbell, **Microscopy & Microanalysis** 10, 28 (2004).
15. "Self-catalyst branch Growth of SnO2 nanowire Junctions" Y.X. Chen, L.R Compbell, and **W.L. Zhou**, **Journal of Crystal Growth** 270, 505 (2004).
16. "Room-temperature Ferromagnetism in Manganese Doped Reduced Rutil Titanium Dioxide Thin Films" Zhenjun Wang, Jinke Tang, Yuxi Chen, Leonard Spinu, and **Weilie Zhou**, **J. Appl. Phys.** 95, 7384 (2004).

Published book chapters

- **Weilie Zhou**, "Fundamentals of Scanning Electron Microscopy"; In Advanced Scanning Electron Microscopy for Nanotechnology; Eds. Weilie Zhou and Zhong Lin Wang, (Springer, New York, 2006). pp.1-40.
- **Weilie Zhou**, "E-beam Nanolithography Integrated with SEM"; In Advanced Scanning Electron Microscopy for Nanotechnology; Eds. Weilie Zhou and Zhong Lin Wang, (Springer, New York, 2006). pp. 120-151.
- **Weilie Zhou** "Doped Transitional Metal for ZnO Nanomaterials"; In Doped ZnO Nanostructures, Eds. Wei Chen, (in press by American Scientific Publisher, 2007).
- **Weilie Zhou**, "Nanomaterials Characterization"; In Microsystems and Nanotechnology, eds Z.L.Wang, (Chinese Science Publishing Company), (2007) (in Chinese).

Presentations

1. "SnO2/Pt Nanocrystals Coated ZnO Nanowires for Highly Sensitive Gas Sensors" Jiajun Chen, Kai Wang, and Weilie Zhou, Fall Meeting, Res. Soc. Fall Meeting, Boston, MA, Nov.26 - Nov.30, 2007.
2. "Room Temperature Ferromagnetism of FeCo-codoped ZnO Nanorods Prepared by Chemical Vapor Deposition" J. J. Chen, Y. Yan, J. J. Liu, A. West□M. H. Yu, and W. L. Zhou, Res. Soc. Fall Meeting, Boston, MA, Nov.26 - Nov.30, 2007.
3. "Diluted Magnetic Semiconductor Metal Oxide Nanowires Synthesis and Spintronic Nanotransistor Fabrication" Weilie Zhou, Jiajun Chen, Jingjing Liu, Kai Wang, 2007 China Nano. Beijing, China June 3-5, 2007.
4. "Room Temperature Ferromagnetism of Mn Doped ZnO Aligned Nanowire Arrays with Temperature Dependent Growth", Jingjing Liu, Amber O. West, Minghui Yu, and Weilie Zhou, Mat. Res. Soc. Spring Meeting, April 9-13, 2007, San Francisco Marriott, San Francisco, CA.
5. "Nanowire Based Electromechanical Switch" Renhai Long, Jiajun Chen, and

Weilie Zhou, Res. Soc. Fall Meeting, Boston, MA, Nov.27 - Dec.01, 2006.

6. "Synthesis and Magnetic Properties of In2-xNixO3 Nanowires" Kai Wang, Jiajun Chen, and Weilie Zhou, Res. Soc. Fall Meeting, Boston, MA, Nov.26 - Nov.30, 2007.
7. "Room Temperature ZnO Nanaostructures for Spintronics Application" Weilie Zhou, Jingjing Liu, Jiajun Chen, and Minghui Yu, Mat. Res. Soc. Fall Meeting, Boston, MA, Nov.27 - Dec.01, 2006.
8. "Nanostructure and EELS Characterization of Diluted Magnetic Semiconductor Zn1-xCoxO Nanoneedles", W.L. Zhou, J.J. Chen, K. Sun, and L.M. Wang, Microscopy & Microanalysis Conference, July 30-Aug.5, Chicago, 2006.
9. "Doped ZnO Nanowire Arrays for Spintronics Application" Weilie Zhou, Jiajun Chen, Jingjing Liu, and Minghui Yu, Mat. Res. Soc. Fall Meeting, Boston, Nov.27-Dec.1, 2006.
10. "Synthesis of Room Temperature Diluted Magnetic ZnO Nanowires", Weilie Zhou Joint Japan, Korea and China Symposium on Rare Earth Related Materials, Changchun, China, July 9-11, 2006.
11. "Fabrication of Room Temperature Diluted Magnetic Semiconductor ZnO Nanowire Arrays", Weilie Zhou, Jingjing Liu, and Jiajun Chen, Mat. Res. Soc. Spring Meeting, San Francisco, April 17-21, 2006.
12. "Diluted Magnetic Semiconductor Zn(Mn)O Nanowire Arrays from a Self-formed ZnO Substrate" Jingjing Liu, Minghui Yu, and Weilie Zhou, Mat. Res. Soc. Spring Meeting, San Francisco, April 17-21, 2006.
13. "Fabrication of Mn Doped ZnO Diluted Magnetic Semiconductor Nanostructures by Chemical Vapor Deposition" J.J. Liu, M.H. Yu, and W.L. Zhou, 50th Magnetism and Magnetic Materials Conference, Oct.30-Nov.3, San Jose, California, 2005
14. "Co-doped ZnO Nanowire Fabrication by Chemical Vapor Deposition" Amber West, Jingjing Liu, Jiajun Chen, Minghui Yu and Weilie Zhou, 2005 International Congress of Nanotechnology, Oct.31-Nov.3, San Francisco, 2005
15. "One-dimensional Diluted Magnetic Semiconductors Prepared by Laser-assisted Thermal Evaporation", Jiajun Chen, Lynn Morlier, and Weilie Zhou, International Congress of Nanotechnology, Oct.31-Nov.3, San Francisco, 2005
16. "Electric Properties Measurement of Mn Doped ZnO Aligned Nanoneedles Using Nanomanipulators in-situ FESEM" J.J. Liu, J.J. Chen, M. Zhu and W.L. Zhou, International Congress of Nanotechnology, Oct.31-Nov.3, San Francisco, 2005
17. "E-beam Nanolithographically Patterned Metal Oxide Nanowire Arrays for Highly

Sensitive Gas Sensors" L. Campbell A. D., D. Smith, G. May, L. Caliste, Y. Chen, and W. L. Zhou, Microscopy and Microanalysis 2005, Hawaii, Aug.1-5 (2005).

18. "Electron Transport Property Measurement of Metal Oxide Nanowire Based Nanodevices Using Nanomanipulators In-Situ FESEM", Weilie L. Zhou, Mo Zhu and Yuxi Chen, Microscopy and Microanalysis 2005, Hawaii, Aug.1-5 (2005).
19. "ZnO Nanostructures synthesized visa Double-tube Vapor Phase Transport for Gas Sensing Applications", Y. X. Chen, L.J. Campbell, and W. L. Zhou. Mat. Res. Soc. Spring Meeting, San Francisco, March 28 - April 1, 2005
20. "Fabrication of Magnetic Hollow Silica nanostructures for Bio-Application" W.L. Zhou, L. Shao, D. Crunta, and J.F. Chen, C.J. O'Connor, Mat. Res. Soc. Spring Meeting, San Francisco, March 28 - April 1, 2005
21. "Fabrication and New Applications of Nanomagnetic Structures", Weilie Zhou; Chen Chen, Lesley Campbell Anglin, Volodymyr Golub, Andriy Vovk, and Leszek Malkinski. Mat. Res. Soc. Fall Meeting, Boston, MA, Nov.29 - Dec.02, 2004.
22. "Multiple Branched SnO2 Nanowire Junction" W.L. Zhou, Y. Chen, L. R. Compbell, 61th Annual Meeting, Microscopy Society of America, Savannah, Georgia, Aug 1-5, 2004.

Participants

1. Dr. Chen Chen
2. Dr. Mo Zhu
3. Dr. Yuxi Chen
4. Dr. Minhui Yu
5. Mr. Jiajun Chen
6. Ms. Raven Anglin
7. Ms. Jingjing Liu

(2) MAGNETO-OPTICS OF NANOMAGNETIC MATERIALS – Dr. Kevin Stokes

SCOPE

This project explored the integration of chemically-synthesized nanoparticles and nanowires with planar nanostructures defined by electron-beam (e-beam) nanolithography. In addition optical, magnetic and magnetic-optical properties of the structures were investigated to assess the possibility of using such structures as photonic device components. The research included the participation of IBM T.J. Watson Research Center through principle investigator Chris Murray and a post-doc to bridge the research efforts between UNO and IBM.

The primary objectives were to create a process for producing thin films using chemically-synthesized nanoparticles; to pattern this films with electron-beam nanolithography; investigate the magnetic and magneto-optical properties of the nanoparticle assemblies.

MAJOR ACCOMPLISHMENTS

- Demonstrated nanometer-scale patterning of a magnetic nanoparticle film. Films of magnetite (Fe_3O_4) nanoparticles were fabricated using electric-field assisted layer-by-layer assembly with a transparent polyelectrolyte. Produced features down to 50 nm using electron-beam lithography.
- Completed a study of the magneto-optics of closely spaced nanoparticles. Identified novel near-field interaction effects (as a function of interparticle distance) in the magneto-optical response.
- Developed a theory of the near-field optical interactions in nanoparticles to account for the observed magneto-optical response. Theory includes a redefinition of Faraday rotation applicable to scattering from nanostructures and predicts spectrally-specific enhancements for coupled noble-metal/magnetic nanoparticle assemblies which depend on nanometer-scale geometries.
- Successfully synthesized cobalt ferrite nanoparticles with varying cobalt concentration and characterized the magneto-optical response of the nanoparticles.
- Data collected contributed to the funded NSF Grant *Novel Chiral Architectures of Magnetic Nanowires,* Lead PI: L. Malkinski and Co-PI: K.L. Stokes. The experimental data and theory were also used in the DoD EPSCoR proposals *Advanced Magnetic Nanocomposites for Wireless Communications and Optoelectronic Applications* (2006) and *Chiral Nanowire Composites as Negative Index Materials* (2007) and the National Science Foundation proposals *Magneto-Optics of Coupled Nanomagnetic-Noble Metal Structures* (2005) and *Magneto-optical Effects in Coupled Nanometer-Scale Structures* (2004).

RESULTS

Master's Degrees Earned

Damon Smith, M.S. in Physics, May 2005. Thesis: "Magneto-Optic Spectroscopy and Near-Field Optical Coupling in Nanoparticle Composite Materials"

Byron L. Scott, M.S. in Applied Physics, December 2007. Thesis: "Magneto-Optical Study of Cobalt Ferrite Nanoparticles"

Papers Published (direct result of this funding)

D.A. Smith and K.L. Stokes, "Discrete Dipole Approximation for Magneto-Optical Scattering Calculations," *Optics Express* **14**:5746-5754 (2006).

J.-S. Jung, Y.-K. Jung, E.-M. Kim, S.-H. Min, J.-H. Jun, L. M. Malkinski, Yu. A. Barnakov, L. Spinu and K. L. Stokes, "Synthesis and magnetic characterization of

$ZnFe_2O_4$ nanostructure in AAO template," *IEEE Trans. Magn.* **41**:3403-3405 (2005).
D.A Smith, Yu. A. Barnakov, B.L. Scott, S.A. White and K.L. Stokes, "Magneto-Optical Spectra of Closely-Spaced Magnetite Nanoparticles," *J. Appl. Phys.* **97**:10M504 (2005).
J.-S. Jung, K.-H. Choi, S.-L. Oh, Y.-R. Kim, S.-H. Lee, D. A. Smith, K.L. Stokes, L. Malkinski, and C.J. O'Connor, "$CoFe_2O_4$ Nanostructures with High Coercivity," *J. Appl. Phys.* **97**:10F306 (2005).

Presentations

"Magneto-Optical Study of Cobalt Ferrite Nanoparticles," B.L. Scott and K.L. Stokes, to be presented at the 2008 TMS Annual Meeting & Exhibition, New Orleans, LA.
"Magneto-Optics of Closely-Spaced Magnetite Nanoparticles," K.L. Stokes and D.A. Smith, presented at Southeastern Section of the American Physical Society, Gainesville, FL, Nov. 2005.
"Magneto-optics of Magnetite Nanoparticles," D.A. Smith, B.L. Scott, and K.L. Stokes, Poster presented at the 8th Annual DARPA-AMRI-Industry Symposium, New Orleans, LA. February 2005.
"Synthesis and Magneto-Optical Properties of Cobalt Ferrites," B.L. Scott, D.A. Smith and K.L. Stokes, Poster presented at the 8th Annual DARPA-AMRI-Industry Symposium, New Orleans, LA. February 2005.

PARTICIPANTS

The following people have contributed to this project.

Dr. Kevin L. Stokes, Co-principle investigator
Damon Smith, Graduate Student
Byron L. Scott, Graduate Student
Jeff Anderson, High-school teacher/graduate student
Dr. William Green, Post-doctoral Research Associate, IBM T. J. Watson Research Center

(3) Developing Nanotechnology of Magnetoresistive Structures for Spintronic Devices – Dr. Leszek Malkinski

Contributors:

Dr. Leszek Malkinski (head of the group)
Dr. Andriy Vovk (postdoctoral researcher)
Donald Scherer II (graduate student)

Project Goals and Objectives:

To develop materials and nanolithographic techniques to fabricate magnetoresistve structures for nanoscale devices. The structures of interest include giant magnetoresistive and spin tunneling structures. Also, an important part of the project was to establish measuring techniques to measure spin-dependent transport in nanostructures.

Realization of the Project and Results:

A measuring system has been designed and built at AMRI to investigate magnetoresistance of the spin -tunneling junctions with submicrometer dimensions. Precise measurements of magneto-transport properties of nanostructures usually require complex multistep lithographic processes to fabricate electrical leads to the nanostructure. A more convenient solution was proposed which minimizes number of elaborate lithographic processes and essentially eliminates the electric leads. The tunneling junctions can be fabricated in the form of nanosized pillars. Because of small area of the tunneling junction its resistance was estimated to be in the range form hundreds to thousands of ohms. Because the resistance of the leads is typically a fraction of ohm it makes possible to measure the resistance of the junctions using two-probe (or two point) method. Existing atomic force microscope was modified to enable this kind of measurements. The semiconducting AFM tip was replaced by a conductive one and the conductive cantilever was replaced. The conductive atomic force microscope with external electronic instruments was able to find nanoscale objects, make a contact with them, provide a bias and measure the current flowing through the object. Phase-sensitive measurements with two lock-in amplifiers replaced originally proposed DC current measurements in order to improve the signal to noise ratio. The works on the measuring system resulted in Masters in Applied Physics degree of the graduate student supported through this grant.

The theoretical works of W. Butler et al. predicted large tunneling magnetoresistance effect in tunneling junctions with MgO barrier. Initial experimental results reported S. Parkin's and S. Yuasa's groups demonstrated that, indeed, the TMR effect in the micron size junctions exceeds the best results (in the junction with alumina barriers) by a factor of two. We expected that reduced size of the junctions should further increase this effect because of smaller number of defects in the small-area barrier.

In addition to physical deposition techniques, such as magnetron sputtering, patterning of the nanopillars was a crucial part of the fabrication process. The patterning of magnetic films was done by the means of the field emission scanning electron microscope with an electron beam writer. Various patterns in the form of magnetic dots, stripes and perforated films have been fabricated by electron beam writing followed by the lift off technique. The size of the smallest structures was 100 nm. Examples of the structures are presented in Figure 1.

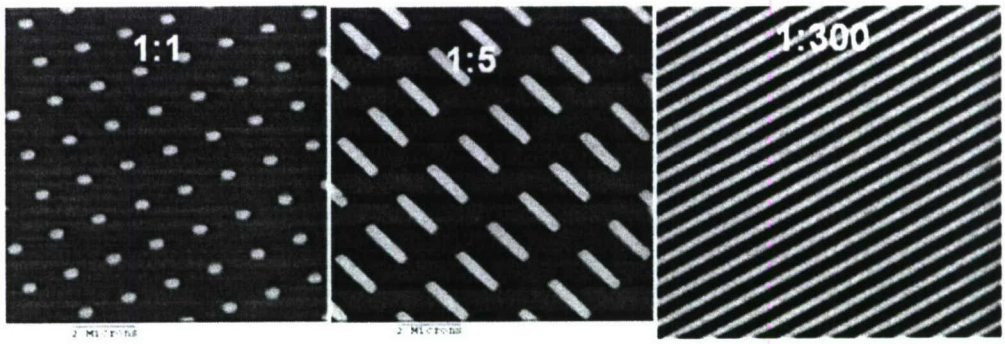

Figure 1. Examples of patters of magnetic dots and stripes fabricated at AMRI using electron-beam writing

Magnetization processes in such structures at quasi-static conditions and at high frequencies (in microwave range) have been carried out using SQUID magnetometer (Quantum Design) and the ferromagnetic resonance system (Brucker EPS system). The shape anisotropy of the patterned objects as well as interactions among neighboring objects in the arrays were both found significant for the switching fields of the tunneling junctions. Improved quality of the junctions could be achieved by replacing the lift-off technique by the ion milling, which or other dry etching process. The ion milling system available at CAMD – LSU, has experienced damage and has only recently been repaired. This fact delayed the final stage of fabrication of the junctions. The efforts to do competitive research in this area will be enhanced by the new system for ion milling funded by Louisiana Board of Regents grant. This system will be installed at AMRI cleanroom in the middle of 2008.

Giant magnetoresistance effect was investigated in NiMnGa shape memory alloys. Single crystals of these alloys do not exhibit magnetoresistance, however alloys fabricated by pulsed laser deposition in the form of nanogranular films showed significant magnetoresistance effect (especially at cryogenic temperatures) related to their morphology and complex spin structure.

In the final phase of the project Fe-doped TiO thin films have been fabricated in collaboration with Prof. Jinke Tang from the Department of Physics, UNO. The films showed room temperature ferromagnetism and therefore are suitable for applications in spintronics.

The partial results on the research have been reported in several presentation on national and international conferences on magnetism and were published in several articles listed below.

List of Relevant Publications

- "Magnetic Behavior of Fe3O4 nanostructure fabricated by template method", K-H. Coi, S.-H. Lee, Y.-R. Kim, L. Malkinski, A. Vovk, Y. Barankov, J.-H.Park, Y.-K Jung, J.S. Jung.Accepted for publication in J. of Magn. and Magn. Mater. 2006

- Magnetic properties of structurally confined FePt nanoparticles within mesoporous nanotubes J.-S. Jung, J.-H. Lim, A. Vovk, L. Malkinski, K.-H. Choi, Y.-R. Kim, S.-L. Oh, J.-H. Jun Accepted for publication in J. Magn. Magn. Mater. 2006
- "Electrodeposition of Ni nanowires in AAO membrane on silicon wafer substrate", J.-S. Jung, L. Malkinski, A. Vovk, M. yu, J.-H. Lim, J.H. Nam and S.-H. Min, accepted to RSC (2006)
- "Magnetic properties of nickel nanostructures grown in AAO membrane", S.-L. Oh, Y.R. Kim, L. Malkinski, A. Vovk, S.L. Whittenburg, E.-M. Kim and J.-S. Jung., accepted for publication in J. Mgn. Magn. Mater. 2006
- "Preparation, structural characterization, and dynamic properties investigation of permalloy antidot arrays" Vovk A, Malkinski L, Golub V, Whittenburg S, O'Connor C, Jung JS, Min SH J. Appl. Phys. 97 (10): Art. No. 10J506 Part 3, (2005)
- "Magnetic and transport properties of NiMnAl thin films" A. Vovk , M.H. Yu, L. Malkinski , C. O'Connor , Z.J. Wang , E. Durant , J.K. Tang , V. Golub , J. Appl. Phys. 99 (8) 08R503 (2006)
- "Structural confinement effects of an amorphous magneto-semiconductor within nanochannels" W.S. Chae , K.H. Choi , Y.R. Kim , J.S. Jung , L. Malkinski , C.J. O'Connor J. Chin. Chem. Soc. 53 (1): 209-217 (2006)
- "Investigation of permalloy antidot arrays deposited on anodic alumina substrates" Vovk AY, Golub VO, Malkinski L, C.J. O'Connor CJ, J.S. Jung Met. Fiz. & Nov. Tek. 28 (2): 259-266 FEB 2006
- "Synthesis and magnetic characterization of ZnFe2O4 nanostructure in AAO template" J.-S. Jung , Y.-K. Jung , E.M. Kim, S.F He. S.H. Min, J.H. Jun , L. M. Malkinski , Y Barnakov, L. Spinu L, K. Stokes, IEEE Trans. Magn 41 (10): 3403-3405 (2005)
- "Magnetotransport in NiMnGa thin films " A. Vovk , L. Malkinski , V. Golub , C. O'Connor , Z.J. Wang , J. K. Tang J. Appl. Phys. 97 (10) 10C503 (2005)
- "CoFe2O4 nanostructures with high coercivity ",J.-S. Jung , J.-H. Lim, K.-H. Choi, S.-L. Oh, Y.-R. Kim , S.-H. Lee, D.-A. Smith, K.L. Stokes , L. Malkinski , O'Connor CJ, J. Appl. Phys. 97 (10) 10F306 (2005)
- L. M. Malkinski, M. Yu, A.Vovk, D. Scherer II, Z. Davis, S. Whittenburg, L. Spinu, and J.-S. Jung, "Microwave absorption of patterend arrays of nanosized magnetic stripes with different aspect ratios," J. Appl. Phys, 101, (2007) 09J110 (1-3)
- M. Yu, L. Malkinski, S.L. Whittenburg, W. Zhou, and L. Spinu, "Size and Py film thickness dependencies of ferromagnetic resonance in nanoscale antidot arrays," J. Appl. Phys.101 (2007) 09F501(1-3)

List of Presentations

- Microwave absorption of nanolithograpically defined arrays of magnetic rods" L. Malkinski, A.Vovk, M.Yu, D. Scherer, W. Zhou and S. Whittenburg. 50th Annual Conference on Magnetism and Magnetic Materials, San Jose, Ca, Oct 30-Nov 3, 2005

- "Electrodeposition of Ni nanowires in AAO membrane on Silicon wafer substrate", J.Jung, J. Nam, S. Min, A. Vovk, M. Yu, L. Malkinski. 50th Annual Conference on Magnetism and Magnetic Materials, San Jose, Ca, Oct 30-Nov 3, 2005
- "Magnetic properties of structurally confined FePt nanoparticles within mesoporous nanotubes", J.-S. Jung, J.-H. Lim, A. Vovk, L. Malkinski, K.-H. Choi, Y.-R. Kim, S.-L. Oh, J.-H. Jun, Presented on Int. Conf on Magnetism, Kyoto, Japan Aug. 2006
- "Magnetic Behavior of Fe3O4 nanostructure fabricated by template method", K-H. Coi, S.-H. Lee, Y.-R. Kim, L. Malkinski, A. Vovk, Y. Barankov, J.-H.Park, Y.-K Jung, J.S. Jung. Presented on Int. Conf on Magnetism, Kyoto, Japan Aug. 2006
- Magnetic and transport properties of NiMnAl thin films, A. Vovk, M.Yu, L. Malkinski, C.O'Connor, Z. Wang,E. Durant, J. Tang, V. Golub, 50th Annual Conference on Magnetism and Magnetic Materials, San Jose, Ca, Oct 30-Nov 3, 2006
- Preparation of doped manganites thin films using discrete deposition techniques, A. Tovstolitkin, A. Pogorily, A. Matvienko, A. Vovk, L. Malkinski, Z. Wang, and J. Tang, 50th Annual Conference on Magnetism and Magnetic Materials, San Jose, Ca, Oct 30-Nov 3, 2005
- L. M. Malkinski, M. Yu, A.Vovk, D. Scherer II, Z. Davis, S. Whittenburg, L. Spinu, and J.-S. Jung, "Microwave absorption of patterend arrays of nanosized magnetic stripes with different aspect ratios," Presented at Joint MMM/INTERMAG conference in Baltimore Jan 2007
- M. Yu, L. Malkinski, S.L. Whittenburg, W. Zhou, and L. Spinu, "Size and Py film thickness dependencies of ferromagnetic resonance in nanoscale antidot arrays,". Presented at Joint MMM/INTERMAG conference in Baltimore Jan 2007

(4) Microstructural Investigation of Electrode Materials used in Rechargeable Li-ion Batteries – Dr. Heike Gabrisch

Rechargeable Li-ion batteries serve as power source for applications in many portable electronic devices (cell phones, lap top computers). Their working principle is based on the reversible intercalation of Li-ions in the van-der-Waals gaps into lattice sites of the active material at both electrodes and the shuttle of the Li-ions between the two electrodes during charge and discharge. The storage and removal of Li-ions from the host lattice are accompanied by reversible changes in the crystallographic and electronic structure. Additionally irreversible changes are observed in the lattice of the intercalation compounds with increased cycle life. Those are attributed to the observed capacity loss of the battery.

Our project focuses on the study of electrode materials by Transmission Electron Microscopy (TEM) techniques. This includes the characterization of irreversible changes observed after electrochemical cycling or ageing at elevated temperature in the charged (lithium depleted) state. The use of single crystal diffraction in a TEM overcomes the

difficulty of distinguishing between closely related structures that is met in x-ray diffraction studies. At the same time image information and structural details of different regions within one powder particle are obtained.

We developed a method for the study of lattice parameters in Li_xCoO_2 compounds by Convergent Beam Electron Diffraction. A potential application of the localized lattice parameter measurement is to monitor lithium gradients within single crystals making use of the lattice extension that accompanies lithium removal from fully lithiated $LiCoO_2$. This project includes the growth and chemical delithiation of single crystalline $LiCoO_2$ as a source of adequate TEM specimen. More application oriented projects were carried out in collaboration with Dr. R. Yazami at the California Institute of Technology. We studied the crystallographic changes in commercial $LiCoO_2$ and $Li_2Mn_2O_4$ cathodes after ageing at elevated temperatures. In the aged particles we identified i. the formation of a cubic spinel phase on $LiCoO_2$ particles, ii. a tetrahedral phase on $Li_2Mn_2O_4$ particles. Both newly formed phases are detrimental for the electrochemical properties of the respective cathodes. In collaboration with Dr. M.M. Doeff at Lawrence Berkeley National Laboratory we investigated carbon coated $LiFePO_4$ particles that are being developed for cathodes in electric and hybrid vehicles. Using Energy Filtered Imaging we proved that the addition of in-situ carbon leads to the formation of a continuous surface film. Investigations of cycled particles showed that the surface films are stable. The repeated lithium insertion and de-intercalation leads to the formation of fractures parallel to low indexed lattice planes. A dislocation-based model can explain the observed fracture surfaces.

Personnel at AMRI supported through this grant: Karin Pruessner, post-doctoral scholar, Qingfeng Xing (postdoctoral scholar, partially supported), Mary Kombolias (grad. student, partially supported), Tanghong Yi (grad. student, partially supported), Fabian Schmitz (visiting grad. student).

Supplemental funding student support was obtained from The Louisiana Board of regents, contract LEQSF(2004-07)-RD-A-36, funding for post doctoral salary was received from the University of New Orleans.

M. Kombolias and Tanghong Yi graduated with a Masters degree doing research for this project.

Conference Contributions

1. *"Localized lattice parameter measurements in Li_xCoO_2 particles by transmission electron microscopy",* H. Gabrisch, Q. Xing, T. Yi, **212th Meeting of the Electrochemical Society**, Washington, DC, October 7-12 2007.
2. *"Investigation of Li_xCoO_2 phases produced by heat treatment of delithiated $LiCoO_2$ powders",* T. Yi, M. Kombolias, H. Gabrisch, DARPA UNO/AMRI Review (DARPA Mardi Gras Review), New Orleans, February 6 2007.
3. *"The effect of charge discharge cycling and chemical delithiation on $LiFePO_4$"*, H. Gabrisch, DARPA UNO/AMRI Review (DARPA Mardi Gras Review), New Orleans,

February 6 2007.

4. *"TEM observations of changes in $LiCoO_2$ with delithiation"*, Q. Xing, T. Yi, H. Gabrisch, DARPA UNO/AMRI Review (DARPA Mardi Gras Review), New Orleans, February 6 2007.
5. *"Determination of c lattice parameter in $LiCoO_2$ by Convergent Beam Electron Diffraction"*, Q. Xing and H. Gabrisch, **206th Joint International Meeting, 210th Meeting of the Electrochemical Society**, Cancun, Mexico, October 29-Novemver 3 2006.
6. *"TEM studies of carbon coated $LiFePO_4$ after charge discharge cycling"*, H. Gabrisch, J. Wilcox, and M. Doeff, **206th Joint International Meeting, 210th Meeting of the Electrochemical Society**, Cancun, Mexico, October 29-Novemver 3 2006. (Invited)
7. *"Investigation of Li_xCoO_2 phases produced by heat treatment of delithiated $LiCoO_2$ powders"*, T. Yi, M. Kombolias, H. Gabrisch, **206th Joint International Meeting, 210th Meeting of the Electrochemical Society**, Cancun, Mexico, October 29-Novemver 3 2006.
8. "*Comparison of carbon coated $LiFePO_4$ before and after charge discharge cycling*" H. Gabrisch, J. Wilcox, and M. Doeff, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006. (Invited)
9. *"Change of Lattice Parameters in Li_xCoO_2 Measured by Convergent Beam Electron Diffraction"*, Q. Xing, T. Yi, and H. Gabrisch, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006.
10. *" Investigation of Li_xCoO_2 phases produced by heat treatment of delithiated $LiCoO_2$ powders"*, T. Yi, M. Kombolias, H. Gabrisch, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006.
11. *"Transition Metal Oxides in Rechargeable Li-ion Batteries"*, **Final AMRI-DARPA Review**, Heike Gabrisch, University of New Orleans, September 2006.
12. *"Comparison of lattice parameters in Li_xCoO_2 compounds obtained from the same parent $LiCoO_2$ powder"*, Qingfeng Xing and Heike Gabrisch, **DARPA review**, New Orleans, July 14 2006.
13. *"Synthesis and Characterization of Cathode Materials for Li Ion Batteries"*, Marca Doeff, James Wilcox and Juliette Saint, **The 2006 Batteries for Advanced Transportation Technologies Annual Peer Review (Department of Energy)**, Lawrence Berkeley National Laboratory, Berkeley, California, June 6-8, 2006 (acknowledged collaborator)
14. *"Distribution of lattice constants in $LiCoO_2$ measured by CBED"* Qingfeng Xing and Heike Gabrisch, **DARPA and AMRI review**, New Orleans, March 18 2006
15. **208th ECS Meeting,**Los Angeles, CA, October 16-21 2005, Rachid Yazami, Yasunori Ozawa, Shu Miao, Brent Fultz and Heike Gabrisch : *Isolating the O1 CoO_2 phase*
16. **56th Annual Meeting of the International Society of Electrochemistry**, Busan,

Korea, September 25-30 2005, H. Gabrisch, Y. Ozawa, R. Yazami, *Crystallographic changes in $LiCoO_2$ and $LiMn_2O_4$ cathodes observed by TEM after self-discharge at elevated temperatures*

17. **3rd ICMAT and 9th International Conference on Advanced Materials (IUMRS-ICAM)**, Singapore, July 3-5 2005, Karin Pruessner, Heike Gabrisch , *Experimental Evidence for a New Ordered Structure in the System Li-Co-O – Electron Diffraction Studies on Cycled and De-Lithiated $LiCoO_2$*
18. **Solid-Solid Phase Transformations in Inorganic Materials 2005,** Phoenix, AZ, May 29-June 3 2005, H. Gabrisch, Y. Ozawa, R. Yazami, *Phase transformations in transition metal oxide cathodes in Li-ion batteries*
19. **207th Meeting of the Electrochemical Society,** Quebec City, Canada, May 15-20 2005, H. Gabrisch, Y. Ozawa, R. Yazami, *Effect of thermal ageing on the crystal structure of $LiCoO_2$ and $LiMn_2O_4$ cathodes for rechargeable Li-ion batteries*
20. **Joint International Meeting of the Electrochemical Society,** Honolulu, Hawaii, October 3-8 2004 , Karin Pruessner, Heike Gabrisch, Rachid Yazami, *Phase Transformations during High Voltage Charging of $LiCoO_2$ Cathodes*
21. **21rst International Battery Seminar, Primary and Secondary Batteries and Small Fuel Cells** , Fort Lauderdale, FL, March 8-11 2004, Karin Pruessner, Heike Gabrisch, *Crystallographic Characterization of Cathode Materials for Rechargeable Li-Ion Batteries*
22. **204th Meeting of the Electrochemical Society,** Orlando, FL, October 12-17 2003. H. Gabrisch, R. Yazami, and B. Fultz, *In-situ observations of phase transformations in $Li_{(1-x)}CoO_2$ - an electron diffraction study*

Publications

1. *"TEM Studies of Carbon Coated $LiFePO_4$ After Charge Discharge Cycling"*, H. Gabrisch, J. Wilcox, M. Doeff, ECS Transactions, Vol. 3, 36, 29-36 (2007).
2. *"Investigation of Li_xCoO_2 Phases Produced by Heat Treatment of Delithiated $LiCoO_2$ Powders"*, T. Yi, M. Kombolias, H. Gabrisch, ECS Transactions, Vol. 3, 36, 145-151, (2007).
3. *"Determination of c-Lattice Parameter of $LiCoO_2$ by Convergent-Beam Electron Diffraction"*, Q. Xing, T. Yi, H. Gabrisch, ECS Transactions, Vol. 3, 27, 83-87, (2007).
4. "*Comparison of carbon coated $LiFePO_4$ before and after charge discharge cycling*" H. Gabrisch, J. Wilcox, and M. Doeff, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006.
5. *"Change of Lattice Parameters in Li_xCoO_2 Measured by Convergent Beam Electron Diffraction"*, Q. Xing, T. Yi, and H. Gabrisch, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006.
6. *" Investigation of Li_xCoO_2 phases produced by heat treatment of delithiated LiCoO2*

powders", T. Yi, M. Kombolias, H. Gabrisch, **7th Louisiana Materials and Emerging Technologies Conference**, Baton Rouge, Oct.23-24 2006.

7. *"Crystal Structure Studies of Thermally Aged $LiCoO_2$ and $LiMn_2O_4$ Cathodes"* Heike Gabrisch, Yasunori Ozawa, Rachid Yazami Electrochimica Acta, 52, 1499-1506 (2006).
8. Heike Gabrisch, James D. Wilcox, and Marca M. Doeff, *"Carbon Surface Layers on a High-Rate $LiFePO_4$"*, Electrochemical and Solid-State Letters, 9, A360 (2006).
9. Heike Gabrisch, Yasunori Ozawa, Rachid Yazami, *"Phase transformations in $LiCoO_2$ a $LiMn_2O_4$ used in cathodes of rechargeable Li-ion batteries"*, Solid to Solid Phase Transformations in Inorganic Materials, Vol.2, p. 1035, Editors: J.M. Howe, D.E. Laughlin, J.K. Lee, D.J. Srolovitz, and U. Dahmen, 2005.
10. R. Yazami, Y. Ozawa, H.Gabrisch and B. Fultz, *"Mechanism of electrochemical performance decay in $LiCoO_2$ aged at high voltage"*, Electrochimica Acta, 50, (2-3), 385-90 (November 2004)
11. *"TEM Study of Fracturing in Spherical and Plate-like LiFePO4 Particles,"* H. Gabrisch, J. Wilcox, and M. M. Doeff, Electrochemical and Solid-State Letters, to be printed 11 (3),1-xxxx, (2008)